(12) UK Patent Application (19) GB (11) 2 174 095 A

(43) Application published 29 Oct 1986

(21) Application No 8606595

(22) Date of filing 18 Mar 1986

(30) Priority data

(31) 60/056301 (32) 20 Mar 1985 (33) JP
60/056311 20 Mar 1985

(71) Applicant
Dainichi-Nippon Cables Ltd (Japan),
8-banchi Higashi-Mukojimanishinocho, Amagasaki-shi,
Hyogo-ken, Japan

(72) Inventors
Hiroshi Kato,
Kiyoshi Furukawa,
Kazuhiko Kanemitsuya

(74) Agent and/or Address for Service
Fitzpatricks, 4 West Regent Street, Glasgow G2 1RS

(51) INT CL[4]
C08K 3/18 C08L 23/04

(52) Domestic classification (Edition H):
C3K 102 123 124 125 127 128 221 222 292 EB
C3W 207 217 218 219
U1S 1362 1551 3011 3045 C3K

(56) Documents cited
GB A 2163167
GB A 2156825
GB A 2041960
GB 1561016
GB 1540400
GB 1479083
GB 1445939
EP A1 0077055
EP A1 0062252
US 4193911
US 3936403
US 3912671

(58) Field of search
C3K
C3V

(54) Flame-retardant resin compositions

(57) Flame-retardant resin compositions comprise:
(A) 100 parts by weight of a base polymer containing a linear polyethylene, and
(B) 50 to about 30 parts by weight of a hydrate of metallic oxide.

The compositions have outstanding flame retardancy and can be made into molded products capable of maintaining satisfactory mechanical characteristics for use over a prolonged period of time.

GB 2 174 095 A

SPECIFICATION

Flame-retardant resin compositions

The present invention relates to flame-retardant resin compositions.

Heretofore known as flame-retardant resin compositions are those prepared using a halogen-containing polymer or by adding an organohalogen flame retardant to non-halogenated polymer. However, the products obtained with use of such flame-retardant resin compositions, although self-extinguishable when taken out from flames, have the drawbacks that they undergo continuous combustion to burn out while in a flame of high temperature as in the event of a fire, they produce a large quantity of smoke, or thermally decompose to release a corrosive or highly toxic acid gas and thus result in a secondary disaster.

On the other hand, attempts have been made to incorporate a halogen-free flame retardant into low density, medium density or high density ethylene homopolymer to overcome the above drawbacks. However, the halogen-free flame retardant needs to be used in a large amount to give fully useful flame retardancy to the resulting resin composition. This results in the following drawbacks. When a large quantity of halogen-free flame retardant is admixed with low density or medium density ethylene homopolymer, the resulting resin composition, when molded or extruded, exhibits seriously reduced mechanical characteristics especially in respect of tensile strength and elongation and is not usable satisfactorily. Further when a large amount of halogen-free flame retardant is incorporated into high density ethylene homopolymer, the molded product prepared from the resin composition obtained similarly shows impaired mechanical characteristics especially in repsect of tensile strength and elongation. Since the mechanical characteristics reduce greatly with time, the molded product fails to retain useful mechanical characteristics. Thus, halogen-free, flame-retardant resin compositions still remain to be developed which are outstanding in flame retardancy and which retain fully useful mechanical characteristics over a prolonged period of time after processing.

An object of the present invention is to provide a halogen-free resin composition having high flame retardancy.

Another object of the present invention is to provide a flame-retardant resin composition which can be molded into a product capable of retaining fully useful mechanical characteristics over a prolonged period of time.

Other features of the present invention will become apparent from the following description.

The flame-retardant resin composition of the present invention comprises (A) about 100 parts by weight of a base polymer containing a linear polyethylene, and (B) about 50 to about 300 parts by weight of a hydrate of metallic oxide.

The linear polyethylene to be used as the component (A) in this invention is a copolymer of an olefin having 4 to 16 carbon atoms and ethylene. It is a substantially linear polyethylene having a density higher than 0.90 but not higher than 0.96 and a melt flow rate (MFR) of 0.1 to 20. The linear polyethylene is prepared, for example, by the following process.

A mixture of ethylene and an olefin having 4 to 16 carbon atoms is polymerized at low pressure in the presence of a catalyst. The mixture ratio between ethylene and olefin is usually about 3 to about 20 parts by weight, preferably about 5 to about 10 parts by weight, of the latter per 100 parts by weight of the former. Examples of useful catalysts are so-called Phillips catalysts typical of which is chromium oxide supported on silica, alumina, zirconia, or silica alumina as a carrier, Ziegler catalysts comprising the combination of compound of a transition metal from Groups IV to VIII of the Periodic Table and an organometallic compound of a metal from Groups I to IV of the Table, etc. More specific examples of useful Ziegler catalysts are combinations of $TiCl_4$ and alkyl aluminums (such as $Al_2(Et_3)Cl_3$, $Al(Et_2)Cl$ and $AlEt_3$). Also useful is a mixture of organomagnesium compound such as $n\text{-}Bu_2Mg.1/6AlEt_3$, the above Ti compound and a organometallic halide. The catalyst is used usually in an amount of about 0.01 to about 50 parts by weight, preferably about 0.05 to about 20 parts by weight, per 100 parts by weight of the mixture of ethylene and olefin having 4 to 16 carbon atoms. The pressure to be applied for the polymerization is usually atmospheric pressure to about 20 atm., preferably atmospheric pressure to about 10 atm. Examples of preferred processes for preparing the linear polyethylene are disclosed more specifically in Unexamined Japanese Patent Publications (Japan Kokai) 51-112891, 55-45722 and 55-113542 and U.S. Patent No. 3,957,448.

Of the linear polyethylenes useful for the present invention, especially suitable are those wherein the olefin comonomer copolymerized with the ethylene chain has about 4 to about 10 carbon atoms. More specifically, the most suitable polyethylenes are those wherein the comonomer is butene-1, octene-1 or 4-methylpentene-1. Further of the useful linear polyethylenes, desirable are those having a density of about 0.91 to about 0.96, preferably about 0.91 to about 0.94, more preferably about 0.911 to about 0.925 as measured according to ASTM D1505. Such polyethylenes are preferably about 0.1 to about 10 in MFR as measured according to ASTM D1238. Examples of such linear polyethylenes are Mitsubishi Polyethylene-LL H20E, F30F and F30H (products of Mitsubishi Petrochemical Co., Ltd.), Ultzex 2020L, 3010F and 3021F (products of Mitsui Petrochemical Industries, Ltd.), DFDA-7540 (products of Union Carbide Corporation), NUCG-5651, GS-650, GRSN-7047 and GRSN-7042 (products of Nippon Unicar Company, Ltd.), Idemitsu Polyethylene-L 0134H and 0234H (products of Idemitsu Petrochemical Co., Ltd.), etc.

According to the present invention, the linear polyethylene can be used in the form of a mixture with a

poly-α-olefin. The poly-α-olefin is a copolymer obtained by polymerizing ethylene with a α-olefin having 4 to 8 carbon atoms in the presence of a Ziegler catalyst and has a density of 0.85 to 0.90 and a MFR of 1 to 10. Of such poly-α-olefins, preferable are those having a density of about 0.86 to about 0.89 and a MFR of about 1 to about 5. Examples of such poly-α-olefins are TAFMER A-4090, A-4085, P-0180 and P-0480 (products of Mitsui Petrochemical Industries, Ltd.), etc.

When the linear polyethylene and the poly-α-olefin are used in mixture, the former to latter ratio by weight is usually about 1-99 : about 99-1, preferably about 95-40 : about 40-60.

Further according to the invention, a polypropylene can be amixed with the linear polyethylene. For example, the polypropylene is one which is about 0.1 to about 5 in MFR and about 0.88 to about 0.91 in density. Examples of useful polypropylenes are BC8-D and EC9 (products of Mitsubishi Petrochemical Co., Ltd.), SB210 ad F301 (products of Mitsui Petrochemical Industries, Ltd.), E250G (product of Idemitsu Petrochemical Co., Ltd.), MK112 (product of Showa Denko K.K.), etc.

When the linear polyethylene and the polypropylene are used as mixed together, the former to latter ratio by weight is usually about 50-99 : about 50-1, preferably about 70-99 : about 30-1.

When a mixture of linear polyethylene, poly-α-olefin and polypropylene is to be used, it is desirable to admix the polyethylene with the poly-α-olefin in the former to latter ratio by weight of 30-70 : 70-30, and to admix about 66 to 150 parts by weight of the polypropylene with 100 parts by weight of the mixture.

The linear polyethylene can be used with an ethylene-vinyl acetate copolymer (EVA) admixed therewith. The EVA to be used is, for example, one which is about 0.2 to about 30 in MFR and about 5 to about 75% by weight in vinyl acetate (VA) content. It is preferably about 0.5 to about 20 in MFR and about 5 to about 50% by weight in VA content. Examples of useful EVA copolymers are EVAFLEX EV660, V527-4, EV-270, V170 and EV45LX (products of Mitsui-Du Pont Polychemical Co., Ltd.), NUC-8450, DQDJ-3269, NUC-3050 and NUC-3270 (products of Nippon Unicar Co., Ltd.), YUKALON-EVA V213K, V403E, V401S and V505 (products of Mitsubishi Petrochemical Co, Ltd.), etc.

Further according to the present invention, an ethylene-ethyl acrylate copolymer (EEA) can be admixed with the linear polyethylene for use. The EEA to be used can be, for example, one which is about 0.2 to about 25 in MFR and about 3 to about 35% by weight in ethyl acrylate (EA) content, preferably about 0.4 to about 20 in MFR and about 5 to about 25% by weight in EA content. Examples of such EEA copolymers are NUC-6220, DQDJ-6182 and NUC-6570 (products of Nippon Unicar Co., Ltd., A170, A270 and T4340-16 (products of Nippon Petrochemical Co., Ltd.), XC-300E and C-400K (products of Mitsubishi Petrochemical Co., Ltd.), A-701, A-702, A-706 and A-710 (products of Mitsui-Du Pont Polychemical Co., Ltd.), etc.

When the mixture of linear polyethylene and EVA or EEA is used, the former to latter mixing ratio is usually about 20-99 : about 80-1, preferably about 50-99 : about 50-1.

The hydrate of metallic oxide to be used as the component (B) of the invention is, for example, a hydrate of oxide of a metal element from Groups Ia, IIa, IIIb, IVa and IVb of the Periodic Table, or a complex salt or compound of such a hydrate and the carbonate of a metal element from Groups Ia and IIa of the table. Examples of useful hydrates are $Al_2O_3{\cdot}nH_2O$ (wherein n is 0.5 to 6, particularly 2.5 to 3.5, hereinafter referred to as "hydrated alumina"), $MgO{\cdot}nH_2O$ (wherein n is 0.5 to 5, particularly 1.5 to 2.5, hereinafter referred to as "hydrated magnesia"), $BaO{\cdot}9H_2O$, $BaO{\cdot}H_2O$, $ZrO{\cdot}2H_2O$, $SnO{\cdot}nH_2O$ (wherein n is 1 to 10), $3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$, $6MgO{\cdot}Al_2O_3{\cdot}H_2O$, $NaCO_3{\cdot}Al_2O_3{\cdot}nH_2O$ (wherein n is 1 to 10), $Na_2O{\cdot}B_2O_3{\cdot}5H_2O$, etc. These hydrates are usable singly, or at least two of them can be used in admixture. In particle size, these metallic oxide hydrates are usually up to about 10 µm, preferably up to abut 5 µm. Generally, particle sizes of about 0.1 to about 5 µm are desirable for use. Of these hydrates, hydrated alumina and hydrated magnesia are especially preferred. Examples of such hydrated aluminas are HYGELLITE H-42M (product of Showa Light Metal Co., Ltd.), B1403 and B1403S (products of Nippon Light Metal Co., Ltd.), etc. Suitable hydrated magnesias are those which are 3 to 15 m^2/g in specific surface area as determined by the BET method and 0% for 5-micron or larger particles in particle size distribution as determined by the Loozex method. Examles of such hydrated magnesias are KISUMA 5B, KISUMA 5A and KISUMA 5E (products of Kyowa Kagaku Kogyo Co., Ltd.), KX-4S (product of Asahi Glass Co., Ltd.), etc.

According to the present invention, usually about 50 to about 300 parts by weight, preferably about 70 to about 200 parts by weight, more preferably about 90 to about 150 parts by weight, of the component (B) is admixed with 100 parts by weight of the component (A). Use of more than 300 parts by weight of the component (B) entails the drawback that the resulting composition exhibits impaired mechanical characteristics. Conversely, with less than 50 parts by weight of the component (B) present, the resin composition has the drawback of reduced flame retardancy.

Preferably, the composition of the present invention has incorporated therein an auxiliary flame retardant such as red phosphorus, zinc borate, titanium dioxide or the like. Examples of useful red phosphorus flame retardants are a wide variety of those commercially available, for example, those at least about 80% in red phosphorus content, up to about 0.8% in weight loss on drying and up to about 7% in plus 74-mesh content. It is desirable that the surface of the red phosphorus particles be covered with a thermosetting resin such as phenolformalin resin or the like. Examples of such red phosphorus flame retardants are NOVARED #120 and NOVARED #120UF (products of Rinkagaku Kogyo Co., Ltd.), etc.

Useful zinc borates are a wide variety of those commercially available. For example, it is desirable to use one represented by the formula $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$, about 2 to about 10 µ in particle size and about 2.6 to about 2.8 g/cm^3 in crystalline density, such as Zinc Borate 2335 (product of Borax Holdings Ltd., England),

etc.

Useful titanium dioxides are those commercially available, for example, those containing at least about 90% of TiO_2 and wholly minus 100 mesh in particle size, or those containing at least about 90% of TiO_2, including none of plus 149-micron particles and having a water content of up to about 0.7%. Examples of such materials are TITONE A-150 and TITONE R-650 (products of Sakai Kagaku Kogyo Co., Ltd.).

According to the present invention, usually about 0.5 to about 50 parts by weight, preferably about 2 to about 25 parts by weight, of the auxiliary flame retardant is used per 100 parts by weight of the component (A). Use of more than 50 parts by weight of the auxiliary flame retardant is not desirable since the resulting resin composition then tends to exhibit lower mechanical characteristics. Conversely, presence of less than 0.5 part by weight of the auxiliary flame retardant results in a tendency for the flame retardancy to fail to exhibit the contemplated effect, hence undesirable.

With the present invention, it is desirable to incorporate an antioxidant into the composition. Examples of useful antioxidants are hindered phenol types and amine types. Various hindered phenol type antioxidants heretofore known are usable which include, for example, [methylene-3-(3,5-di-tert-butyl-4-hydroxyphenol)-propionate]methane (Irganox 1010, product of CIBA GEIGY Corp.), 2,2-thio[diethyl-bis-3-(3,5-di-tert-butyl-4-hydroxyphenol)-propionate] (Irganox 1035, product of CIBA GEIGY Corp.), 4,4′-thiobis(3-methyl-6-tert-butylphenol) SUNTONOX, product of Monsanto Co.), 4,4′-methylene-bis(3,5-di-tert-butylphenol) (lonox 220, product of ICI, England), etc. Various amine type antioxidants heretofore known are also usable, which include, for example, Antioxidant DDA (DDA, product of Bayer AG.), N,N′-di-β-naphthyl-p-phenylenediamine (Nocrac White, product of Ohuchi Shinko Co., Ltd.), N,N′-diphenyl-p-phenylenediamine (Nocrac DP, product of Ohuchi Shinko Co., Ltd), N,N′-diisopropyl-p-phenylenediamine (Antioxidant No. 23, product of E.I. du Pont de Nemours & Co.), etc. These agents are usable singly, or at least two of them are usable in admixture.

The antioxidant is used usually in an amount of about 0.1 to about 5 parts by weight, preferably about 0.2 to about 3 parts by weight, more preferably about 0.3 to about 2 parts by weight, per 100 parts by weight of the component (A). Use of more than 5 parts by weight of the antioxidant fails to produce a noticeably improved effect and is therefore economically undesirable. With less than 0.1 part by weight of the antioxidant present, it is difficult to achieve the intended aging preventing effect, hence undesirable.

It is desirable to incorporate a higher fatty acid or a metal salt thereof into the composition of this invention as an processing aid. Examples of useful fatty acids are stearic acid, oleic acid and the like, while examples of useful metal salts are zinc salt, calcium salt and the like.

The higher fatty acid or metal salt thereof is used usually in an amount of about 0.1 to about 10 parts by weight, preferably about 0.5 to about 5 parts by weight, per 100 parts by weight of the component (A). Use of more than 10 parts by weight of the acid or salt tends to result in the drawback that the resin composition obtained exhibits impaired properties, for example, in respect of mechanical characteristics. Presence of less than 0.1 part by weight of the processing aid fails to produce the contemplated effect.

It is also desirable to incorporate carbon black into the composition of this invention. Examples of useful carbon black materials are furnace black designated N330 to N351 in ASTM code and 100 to 160 cm^3/100 g in DBP oil absorption, and thermal black which is 30 to 50 cm^3/100 g in DBP oil absorption. Such materials include FEF carbon black, HAF carbon black, ISAF carbon black, SRF carbon black, etc. More specific examples are Diablack H and Diablack HS (products of Mitsubishi Chemical Industries, Ltd.), Vulcan-3 and Vulcan-3H (products of Cabot Corp.), Seast H and Seast 3H (products of Tokai Electrode Co., Ltd.), Ketjenblack HAF (product of Ketjen Corp.), etc. Of these, Diablack H and Vulcan-3 are desirable.

According to the present invention, usually about 0.5 to about 40 parts by weight, preferably about 1 to about 20 parts by weight, of carbon black is used per 100 parts by weight of the component (A). Use of more than 40 parts by weight of carbon black is undesirable since the resulting resin composition then tends to exhibit impaired mechanical characteristics. With less than 0.5 part by weight of carbon black present, the composition has difficulty in exhibiting ashing characteristics, hence undesirable.

According to the present invention, it is desirable to incorporate a coupling agent into the composition. Various coupling agents heretofore known are usable which include titanate coupling agents monoalkoxy, neoalkoxy, coordination, chelate or like type and silane coupling agents. Of such titanate coupling agents, desirable are those containing phosphorus, such as tetraisopropyl-di(dioctylphosphite)titanate (KR-41B, product of Kenrich Petrochemicals, Inc.), isopropyl-tris(dioctyl-pyrophosphate)titanate (KR38S, product of the same company), bis(dioctylpyrophosphate)oxyacetatetitanate (KR138S, product of the same company), etc.

Examples of useful titanate coupling agents of the chelate type are di-isostearoyloxyacetatetitanate (KR-101), dicumylphenol aceoxyacetate-titanate (KR-134S), di(dioctylphosphate)ethylene-titanate (KR-212), 4-aminobenzenesulfonyldodecylbenzenesulfonylethylene-titanate (KR-226S) and di(butylmethylpyrophosphate)ethylene-titanate (KR-262ES) which are products of Kenrich Petrochemicals, Inc.

Preferred silane coupling agents are trialkoxy-silanes having a carbon-to-carbon double bond or epoxy group, such as vinyl-tris(β-methoxyethoxysilane) (A172, product of Nippon Unicar Co., Ltd.), γ-methacryloxy-propyltrimethoxysilane (A174, product of the same company), β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (A186, product of the same company), γ-glycidyloxy propyl-trimethoxysilane (SH6040, Toray Silicone Co., Ltd.), etc.

The coupling agent is used usually in an amount of about 0.1 to about 5 parts by weight, preferably about 0.3 to about 3 parts by weight, more preferably about 0.5 to about 2 parts by weight, per 100 parts by weight

of the component (A). Use of more than 5 parts by weight of the coupling agent is not desirable since the resin composition then obtained tends to exhibit lower flame retardancy and lower heat resistance. Use of less than 0.1 part by weight of the coupling agent tends to result in impaired processability.

When the component (A) comprises the aforementioned polypropylene and the linear polyethylene, it is especially desirable to incorporate a copper inhibitor into the composition of this invention. Useful copper inhibitors are a wide variety of those already known, such as N,N'-bis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionyl]hydrazine, [3-(N-salicyloyl)amino-1,2,4-tetrazole], N,N'-dibenzaloxalyldihydrazide, N,N'-disalicylideneoxalylhyrazide, etc. The copper inhibitor is used usually in an amount of about 0.02 to about 5 parts by weight, preferably about 0.1 to about 2 parts by weight, per 100 parts by weight of the polypropylene. Use of more than 5 parts by weight of the inhibitor is not desirable economically since a noticeably increased effect will not be achieved. With less than 0.02 part by weight present, it becomes difficult to obtain the contemplated the effect.

In addition to the foregoing components, fillers, small amounts of organic flame retardants, plasticizers, pigments and the like can be incorporated into the composition of this invention.

Examples of useful fillers are metallic oxides such as zinc oxide, magnesium oxide, beryllium oxide, boron oxide and aluminum oxide, carbonates such as magnesium carbonate and calcium carbonate, silicates (such as clay, talc and feldspar powder), graphite, barium sulfate, lithopone, silicas, kieselguhr, mica powder, siliceous sand, slate powder, asbestos, aluminum sulfate, calcium sulfate, molybdenum disulfide, potassium titanate, etc. Such fillers are used usually in an amount of about 5 to about 200 parts by weight, preferably about 10 to about 150 parts by weight, more preferably about 5 to about 50 parts by weight, per 100 parts by weight of the component (A). Use of more than 200 parts by weight of the filler is not desirable since the resulting resin composition tends to exhibit impaired mechanical characteristics. Use of less than 5 parts by weight of the filler fails to produce the contemplated effect and is not desirable.

Examples of useful organic flame retardants are organobromides such as tris(2,3-dibromopropyl)isocyanurate, 2,3-dibromopropyl methacrylate, pentabromotoluene, decabromodiphenyl ether, tetrabromobisphenol S and 2,2'-bis (4-hydroxy-3,5-dibromophenyl)propane, organophosphorusbromide compounds such as bis(2,3-dibromopropyl)dichloropropyl phosphate, organochlorides such as chlorinated paraffin, dimethyl chlorendate, Dechlorane Plas 25 (product of Hooker Chemical Co., U.S.A.), organophosphorus compounds such as phenylphosphonic acid, di(polyoxyethylene)hydroxymethyl phosphonate, etc. These flame retardants are used usually in an amount of about 0.5 to about 10 parts by weight, preferably about 1 to about 5 parts by weight, per 100 parts by weight of the component (A). Use of more than 10 parts by weight of the organic flame retardant results in an objectionable tendency for the resulting resin composition to produce an increased amount of smoke and an increased amount of toxic hydrogen halide gas when burning. Conversely, presence of less than 0.5 part by weight of the organic flame retardant fails to produce the contemplated effect and is not desirable.

Examples of useful plasticizers are naphthenic and aromatic plasticizers, process oil, phthalates, trimellitates, epoxy resins, etc. Such plasticizers are used usually in an amount of about 0.2 to about 50 parts by weight, preferably about 1 to about 10 parts by weight, per 100 parts by weight of the component (A).

Examples of useful pigments are Phthalocyanine Blue, Chrome Yellow, red iron oxide, etc. These pigments are used usually in an amount of about 0.1 to about 20 parts by weight, preferably about 0.5 to about 10 parts by weight, per 100 parts by weight of the component (A).

The resin composition of the present invention can be used as crosslinked. The composition may be crosslinked using, for example, organic peroxide, electron rays, radiation or water. Preferably the composition is crosslinked with use of an organic peroxide or electron rays.

The composition of the present invention can be prepared by uniformly mixing together specified amounts of the desired components given above by a usual method, using a Banbury mixer, Henschel mixer or the like. Although all the components can be mixed together at the same time, it is desirable to admix the coupling agent along with the filler. When two or more kinds of polymers are used as the component (A), it is desirable to uniformly mix the polymers together and to admix the other components with the mixture.

The composition of this invention can be molded by various known methods for use. For example, the composition is kneaded by a kneader such as a rolling mill and then shaped into the desired form for the contemplated use.

Since the composition of the present invention is essentially free from halogen, the composition will not produce large amount of smoke or release any corrosive gas or acid gas owing to thermal decomposition even if allowed to stand in flames of high temperature, for example, in the event of a fire. Moreover, the composition of this invention is outstanding in flame retardancy, tensile strength, electrical characteristics, resistance to aging, etc. The composition is therefore useful as a building material, material for pipes, hoses, sheets, sheet covers and walls, covering materials for electric wires and cables (for inner insulations and outer sheaths), etc.

Above all, the composition of the invention is well-suited for use as a flame-retardant resin composition for covering insulations and sheaths of electric wires and cables. In such a case, the composition of this invention is used for electrical insulation layers over suitable portions, for example, over conductors or inner semi-conductive layers, of communication cables, power cables, control cables, etc. The composition is usable also for protective layers (sheaths) over suitable portions, e.g., over insulation layers or outer semiconductive layers, of such cables. In these applications, the composition gives the cables high fire

resistance, flame retardancy, etc.

The present invention will be described in greater detail with reference to the following examples.

The specimens prepared in these examples were tested for characteristics by the following methods.

Flame retardancy test

The composition of the invention was kneaded into a uniform mixture by a rolling mill and then molded into a specimen sheet, 3.0 mm in thickness, by a hot press (pressure 100 to 150 kg/cm^2, temperature 180°C, time 10 minutes). The limited oxygen index (LOI) of the sheet was determined according to JIS K 7201 (oxygen index method) to evaluate the flame retardancy.

Mechanical characteristics

The composition was kneaded and molded into specimen sheets, 1 mm in thickness, in the same manner as above. The sheets were checked for the following characteristics.

(1) 100% Modulus (kg/mm^2)... according to ASTM D882.

(2) Tensile strength (kg/mm^2)... according to ASTM D882.

(3) Elongation (%).........according to ASTM D882.

Electrical characteristics (room temperature)

Using a rolling mill, the composition of this invention was kneaded into a uniform mixture, which was then molded into a 1-mm-thick specimen sheet by a hot press (pressure 100 to 150 kg/cm^2, temperature 180°C, time 10 minutes). The ρ value (volume resistivity, ohm-cm) of the sheet was measured according to JIS C 2123.

Aging characteristics

The same specimen sheets as used for testing the electrical characteristics were allowed to stand at 100°C for 10 days and thereafter checked for residual tensile strength (%) and residual elongation (%) according to ASTM D573.

The symbols for components used in the following examples stand for the following.

Base polymers

A-1: linear polyethylene (Ultzex 2020L, product of Mitsui Petrochemical Industries, Ltd., MFR=2.1, density=0.920)

A-2: linear polyethylene (Mitsubishi Polyethylene-LLF30F, product of Mitsubishi Petrochemical Co., Ltd., MFR=1.0, density=0.920)

A-3: linear polyethylene (Ultzex 3010F, product of Mitsui Petrochemical Industries, Ltd., MFR=1.3, density=0.930)

A-4: linear polyethylene (Mitsubishi Polyethylene-LL H20E, product of Mitsubishi Petrochemical Co., Ltd., MFR=0.5, density=0.918)

A-5: linear polyethylene (NUCG-5651, product of Nippon Unicar Co., Ltd., MFR=0.9, density=0.920)

A-6: linear polyethylene (Idemitsu Polyethylene-L 0134H, product of Idemitsu Petrochemical Co., Ltd., MFR=1.0, density=0.920)

A-7: poly-α-olefin (TAFMER A4090, product of Mitsui Petrochemical Industries, Ltd., MFR=3.6, density=0.89)

A-8: poly-α-olefin (TAFMER PO480, product of Mitsui Petrochemical Industries, Ltd., MFR=1.2, density=0.88)

A-9: polypropylene (BC-8D, product of Mitsubishi Petrochemical Co., Ltd.)

A-10: polypropylene (BC-5C, product of Mitsubishi Petrochemical Co., Ltd.)

A-11: polypropylene (SB-210, product of Mitsui Petrochemical Co., Ltd.)

A-12: polypropylene (E-250, product of Idemitsu Petrochemical Co., Ltd.)

A-13: EVA (Evaflex V527-4, product of Mitsui-Du Pont Polychemical Co., Ltd., MFR=0.8, VA content=17 wt.%)

A-14: EVA (NUC-8450, product of Nippon Unicar Co., Ltd., MFR=2, VA content=15 wt.%)

A-15: EVA (Yukalon-EVA V401S, product of Mitsubishi Petrochemical Co., Ltd., MFR=15, VA content=20 wt.%)

A-16: EEA (DPDJ-6182, product of Nippon Unicar Co., Ltd., MFR=1.5, EA content=15 wt.%)

A-17: EEA (A270, product of Nippon Petrochemical Co., Ltd., MFR=1.2, EA content=15.6 wt.%)

A-18: EEA (A710, product of Mitsui-Du Pont Polychemical Co., Ltd., MFR=0.5, VA content=15 wt.%)

Flame retardants

B-1: $Mg(OH)_2$ (KISUMA 5B, product of Kyowa Kagaku Kogyo Co., Ltd.)

B-2: $Mg(OH)_2$ (KX-4S, product of Asahi Glass Co., Ltd.)

B-3: $Al(OH)_3$ (Hygellite H42M, product of Showa Light Metal Co., Ltd.)

B-4: $Al(OH)_3$ (B1403S, product of Showa Light Metal Co., Ltd.)

B-5: $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$

B-6: $6MgO \cdot Al_2O_3 \cdot H_2O$

Additives

C-1: red phosphorus, (Novared #120, product of Rinkagaku Co., Ltd.)

C-2: zinc borate (Zinc Borate #2335, product of Borax Holding Ltd.)

C-3: titanium dioxide (TITONE A150, product of Sakai Kagaku Kogyo Co., Ltd.)

C-4: silane coupling agent (vinyl-tris(β-methoxyethoxysilane), A172, product of Nippon Unicar Co., Ltd.)

C-5: silane coupling agent (γ-methacryloxypropyl-trimethoxysilane, A174, product of Nippon Unicar Co.,

Ltd.)

C-6: titanium coupling agent (isopropyl-tris(dioctylpyrophosphate)titanate, KR38S, product of Kenrich Petrochemicals, Inc.)

C-7: titanium coupling agent (bis(dioctylpyrophosphate)-oxyacetate-titanate, KR138S, product of Kenrich Petrochemicals, Inc.)

C-8: chelate-type titanium coupling agent (di-iso-stearoyloxyacetate-titanate, KR101, product of Kenrich Petrochemicals, Inc.)

C-9: FEF carbon Seast SO, product of Tokai Electrode Co., Ltd.)

C-10: HAF carbon (Diablack H, product of Mitsubishi Chemical Industries, Ltd.)

C-11: HAF carbon (Vulcan-3, product of Cabot Corp.)

C-12: stearic acid

C-13: zinc stearate

C-14: polyethylene wax (Nisseki Uniwax, product of Nippon Petrochemical Co., Ltd.)

C-15: antioxidant (3,5-di-tert-butyl-4-hydroxyphenol)-propionate, Irganox 1035, product of Ciba Geigy Corp.)

C-16: antioxidant (N,N′-di-β-naphtyl-p-phenylene-diamine, Nocrac White, product of Ohuchi Shinko Co., Ltd.)

C-17: antioxidant (N,N′-diisopropyl-p-phenylenediamine, Antioxidant No. 23, product of E.I. du Pont de Nemours & Co.)

C-18: antioxidant (Seenox 412S, Shiraishi Calcium Co., Ltd.)

C-19: antioxidant (tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane, Irganox 1010, product of Ciba Geigy Corp.)

C-20: copper inhibitor (N,N′-bis[3-(3′,5′-di-tert-butyl-4′-hydroxyphenyl)propionyl]hydrazine)

C-21: copper inhibitor (N,N′-dibenzyl oxalylhydrazide)

C-22: copper inhibitor (N,N′-disalicylidene oxalylhydrazide)

C-23: antioxidant (4,4′-dihydroxy-3,3′-di-tert-butyl-5,5′-dimethyl-diphenylsulfide, Nocrac 300, product of Ohuchi Shinko Co., Ltd.)

C-24: organic flame retardant (decabromodiphenyl ether, PLANELON DB-100, product of Mitsui Toatsu Chemicals, Inc.)

C-25: organic flame retardant (aliphatic polycyclic chlorine compound, Deckloran plas 25, product of Hooker Chemical Co.)

C-26: filler (zinc oxide, Active Zinc Oxide No. 1, product of Honjo Chemical Co., Ltd.)

C-27: filler (magnesium oxide, Kyowamag 100, product of Kyowa Kagaku Kogyo Co., Ltd.)

C-28: filler (Dixie Clay, product of R.T. Vanderbilt)

C-29: filler (graphite, product of Tsuchiya Kaolin Kogyo Co., Ltd.)

C-30: filler (barium sulfate, lithopon, product of Sakai Kagaku Kogyo Co., Ltd.)

Example 1

Compositions of the present invention were prepared by mixing together specified amounts (in parts by weight) of the components listed in Table 1 below in the following manner. The base polymer and the flame retardant were uniformly mixed together at a temperature of 130 to 140°C by a rolling mill and then made into a composition in the form of a sheet.

The compositions thus prepared were tested for flame retardancy and elongation by the above-mentioned methods. Table 1 also shows the results.

For comparison, compositions were prepared in the same manner as above except that the base polymers used were A-19, A-20 and A-21 given below. These compositions were also tested for flame retardancy and elongation with the results given in Table 1.

A-19: low density ethylene homopolymer (Yukalon HE-30, product of Mitsubishi Petrochemical Co., Ltd., MFR=0.30, density=0.920)

A-20: medium density ethylene homopolymer (Hizex 6300M, product of Mitsui Petrochemical Industries Ltd., MFR=0.11, density=0.920)

A-21: high density ethylene homopolymer (Hizex 5200S, product of Mitsui Petrochemical Industries Ltd., MFR=0.30, density=0.964)

TABLE 1

	Composition No.								
	1	2	3	4	5	6	7	8	9
A-1	100								
A-2		100							
A-3			100						
A-4				100					
A-5					100				
A-6						100			
A-19							100		
A-20								100	
A-21									100
B-1	100	100	100	100	100	100	100	100	100
Flame retardancy (LOI)	27.2	27.6	27.2	26.8	27.2	27.6	25.2	25.6	26.2
Elongation (%)	450	410	405	510	550	415	93	75	50

Table 1 above shows that when the base polymers used were linear polyethylenes, the resin compositions obtained were excellent in flame retardancy and mechanical characteristics (elongation).

Example 2

Compositions of the present invention were prepared from specified amounts (in parts by weight) of the components listed below in Table 2 by uniformly mixing together the base polymer, flame retardant and other additives at a temperature of 130 to 180°C by a rolling mill and then making the mixture into a sheet.

TABLE 2

Component	Composition No. 10	11	12	13	14	15	16
Base polymer							
A-1	50	50	50	50		20	50
A-2						20	
A-3					60		
A-4							
A-5							
A-6							
A-7	25	25	25			60	
A-8				25	20		
A-9	25						
A-10		25			20		
A-11			25				
A-12				25			50
A-13							
A-14							
A-15							
A-16							
A-17							
A-18							
Flame retardant							
B-1	100	100	120	70	150		100
B-2							
B-3							
B-4						150	
B-5							
B-6							
Other additives							
C-1	5	10	10	10			
C-2							
C-3							
C-4			1				
C-5		0.1					
C-6							
C-7	1	0.5	1				
C-8				1			
C-9							
C-10							
C-11							
C-12		1		1	1	2	
C-13	2	1	2				
C-14							
C-15							
C-16							
C-17							
C-18	0.3	0.5	0.5	1.0	0.5	0.1	0.3
C-19	0.3	0.5	0.5	1.0	0.5	0.6	0.3
C-20	0.5	0.5				0.3	0.1
C-21			0.5	0.5		0.3	
C-22					0.5		0.1
C-23							
C-24							
C-25							
C-26							
C-27							
C-28							
C-29							
C-30							

TABLE 2 (continued)

Component	Composition No.						
	17	18	19	20	21	22	23
Base polymer							
A-1	50		90	100		50	50
A-2		50			25		
A-3							
A-4							
A-5							
A-6							
A-7	50	50	10		50	50	50
A-8					25		
A-9							
A-10							
A-11							
A-12							
A-13							
A-14							
A-15							
A-16							
A-17							
A-18							
Flame retardant							
B-1	100	100	120	130	150	130	100
B-2							
B-3							
B-4							
B-5							
B-6							
Other additives							
C-1	10	10	10		10	20	10
C-2				10			
C-3					10		
C-4							
C-5							
C-6	1	0.5					1
C-7				2	1		
C-8			1				
C-9							
C-10							10
C-11	10	10	10	5	10		
C-12	2	2	2	2	2		2
C-13							
C-14							
C-15							
C-16							
C-17							
C-18							
C-19							
C-20							
C-21							
C-22							
C-23	1	1	1	1	1	1	1
C-24							
C-25							
C-26							
C-27							
C-28							
C-29							
C-30							

TABLE 2 (continued)

Component	Composition No. 24	25	26	27	28	29	30
Base polymer							
A-1		90	100		50		
A-2	50			25			
A-3						80	
A-4							80
A-5							
A-6							
A-7	50	10		50	50		
A-8				25		10	10
A-9							
A-10							
A-11							
A-12							
A-13							10
A-14							
A-15							
A-16							
A-17							
A-18							
Flame retardant							
B-1	100	120	130	150	130		
B-2						130	130
B-3							
B-4							
B-5							
B-6							
Other additives							
C-1	10	10	5	10	20		
C-2						5	5
C-3							
C-4						0.5	
C-5							0.5
C-6	0.5						
C-7		1		1	0.5		
C-8			2				
C-9							
C-10	10	10	10				
C-11				10	5		
C-12	2	2	2	2		1	1
C-13					1	1	1
C-14							
C-15						1	
C-16							1
C-17							
C-18							
C-19							
C-20							
C-21							
C-22							
C-23	1	1	1	1	1.		
C-24							
C-25							
C-26							
C-27							
C-28							
C-29							
C-30							

TABLE 2 (Continued)

Component	Composition No. 31	32	33	34	35	36	37
Base polymer							
A-1							80
A-2							
A-3			50				
A-4				50			
A-5	80				50		
A-6		80				50	
A-7							
A-8							
A-9							
A-10							
A-11							
A-12							
A-13						10	10
A-14	10						10
A-15		10					
A-16			20				
A-17				20			
A-18					20	10	
Flame retardant							
B-1				100	100	100	
B-2							100
B-3	120	120	120				
B-4				20			
B-5					20		
B-6						20	10
Other additives							
C-1			5	5	5	5	
C-2							5
C-3	5	5					
C-4							0.5
C-5							0.5
C-6			0.5	0.5	0.5	0.5	
C-7			0.5	0.5	0.5	0.5	
C-8							
C-9			5	5	5		
C-10							
C-11							5
C-12	1	2	2	0.5	0.5	0.5	0.5
C-13	1						1
C-14		1	1	5	5	5	
C-15				1	0.5	0.5	
C-16							0.5
C-17	1	1					
C-18		1					
C-19			1	1			
C-20							
C-21							
C-22							
C-23					0.5	0.5	0.5
C-24							2
C-25							
C-26			10				
C-27				10			
C-28					10		
C-29	10	10				10	
C-30							10

TABLE 2 (continued)

Component	38	39	40	41	42
Base polymer					
A-1					
A-2	80				
A-3		80			
A-4			100		
A-5				100	
A-6					100
A-7					
A-8					
A-9					
A-10					
A-11					
A-12					
A-13					
A-14	10				
A-15		10			
A-16	10				
A-17		10			
A-18					
Flame retardant					
B-1					120
B-2	100	100			
B-3					
B-4			120	120	
B-5			5	5	5
B-6	5	5			
Other additives					
C-1			10	10	10
C-2	5	5			
C-3					
C-4					
C-5					
C-6					
C-7					
C-8					
C-9					
C-10			10	10	10
C-11	5	5			
C-12	0.5	0.5			
C-13	1	1	1	1	1
C-14			2	2	2
C-15					
C-16	0.5				
C-17				0.5	0.5
C-18		0.5			
C-19			0.5	0.5	0.5
C-20					
C-21					
C-22					
C-23	0.5	0.5	0.5		
C-24	2				
C-25		2			
C-26					
C-27					
C-28					
C-29					
C-30					

Table 3 below shows the characteristics of the compositions of the invention thus obtained.

TABLE 3

Characteristics	Composition No. 10	11	12	13	14	15	16
Flame retardancy (LOI)	29.4	30.1	31.7	29.4	31.3	32.5	28.9
Mechanical properties							
(1)	0.92	0.88	0.94	0.95	0.87	0.86	0.98
(2)	1.65	1.76	1.66	1.92	1.75	1.66	1.88
(3)	420	490	520	550	505	515	450
Volume resistivity ρ ohm-cm ($\times 10^{15}$)	0.5	0.8	1.2	2.0	0.8	0.5	0.8
Aging properties 100°C, 10 days							
Residual tensile strength (%)	95	96	95	91	88	92	89
Residual elongation(%)	88	89	91	89	87	86	92

TABLE 3 (continued)

Characteristics	Composition No. 17	18	19	20	21	22	23
Flame retardancy (LOI)	30.3	29.8	33.4	33.4	32.0	31.4	31.6
Mechanical properties							
(1)	0.90	0.70	0.80	0.86	0.90	0.58	0.96
(2)	1.35	0.96	1.30	1.38	1.11	1.15	1.38
(3)	500	450	630	400	510	480	450
Volume resistivity ρ ohm-cm ($\times 10^{15}$)	6.0	8.0	0.5	0.7	0.6	1.5	6.0
Aging properties 100°C, 10 days							
Residual tensile strength (%)	100	99	89	96	97	101	101
Residual elongation (%)	95	105	99	92	94	96	96

TABLE 3 (continued)

Characteristics	Composition No. 24	25	26	27	28	29	30
Flame retardancy (LOI)	30.3	34.6	34.6	33.4	35.1	34.6	33.4
Mechanical properties							
(1)	0.72	0.81	0.84	0.93	0.65	0.72	0.79
(2)	1.02	1.40	1.43	1.21	1.11	1.14	1.25
(3)	440	550	405	495	505	420	410
Volume resistivity ρ ohm-cm ($\times 10^{15}$)	7.0	0.4	0.6	0.5	1.2	5.5	5.4
Aging properties 100°C, 10 days							
Residual tensile strength (%)	100	92	94	98	105	94	96
Residual elongation(%)	100	89	91	96	94	92	93

TABLE 3 (continued)

Characteristics	Composition No. 31	32	33	34	35	36	37
Flame retardancy (LOI)	31.6	32.0	31.4	33.4	33.4	34.6	30.3
Mechanical properties							
(1)	0.88	0.84	0.64	0.62	0.65	0.62	0.82
(2)	1.29	1.36	1.21	1.15	1.23	1.20	1.12
(3)	480	475	590	610	605	595	400
Volume resistivity ρ ohm-cm ($\times 10^{15}$)	0.6	0.7	0.7	0.4	0.9	8.6	1.1
Aging properties 100°C, 10 days							
Residiual tensile strength (%)	92	90	101	100	98	106	98
Residual elongation(%)	82	89	92	94	92	95	90

TABLE 3 (continued)

Characteristics	Composition No. 38	39	40	41	42
Flame retardancy (LOI)	29.8	32.0	31.4	32.0	31.4
Mechanical properties					
(1)	0.79	0.86	0.91	0.80	0.88
(2)	1.21	1.30	1.38	1.29	1.40
(3)	425	480	500	525	510
Volume resistivity ρ ohm-cm ($\times 10^{15}$)	1.5	0.9	4.5	4.9	8.0
Aging properties 100°C, 10 days					
Residual tensile strength (%)	92	100	101	105	111
Residual elongation(%)	92	94	89	88	91

Table 3 reveals that the sheets of the present compositions have outstanding characteristics.

CLAIMS

1. A flame-retardant resin composition comprising:
(A) about 100 parts by weight of a base polymer containing a linear polyethylene, and
(B) about 50 to about 300 parts by weight of a hydrate of metallic oxide.
2. A composition as defined in claim 1 wherein the linear polyethylene is used as the base polymer.
3. A composition as defined in claim 1 wherein the base polymer is a mixture of the linear polyethylene and at least one compound selected from the group consisting of poly-α-olefin, polypropylene, ethylene-vinyl acetate copolymer and ethylene-ethyl acrylate.
4. A composition as defined in any one of claims 1 to 3 wherein the linear polyethylene has a density of about 0.91 to about 0.94 as determined according to ASTM D1505 and a melt flow rate of about 0.1 to about 10 as determined according to ASTM D1238.
5. A composition as defined in any one of claims 1 to 4 wherein the hydrate of metallic oxide is at least one compound selected from the group consisting of hydrated alumina, hydrated magnesia, $3MgCO_3 \cdot Mg(OH)_2 . 3H_2O$ and $6MgO \cdot Al_2O_3 \cdot H_2O$.
6. A composition as defined in any one of claims 1 to 5 which comprises 100 parts by weight of the component (A) and about 70 to about 200 parts by weight of the component (B).
7. A composition as defined in any one of claims 1 to 6 further comprising an auxiliary flame retardant.
8. A composition as defined in any one of claims 1 to 7 further comprising antioxidants.
9. A composition as defined in any one of claims 1 to 8 futher comprising a higher fatty acid or a metal salt thereof as a processing aid.
10. A composition as defined in any one of claims 1 to 9 further comprising carbon black.
11. A composition as defined in any one of claims 1 to 10 further comprising a coupling agent.

Printed in the UK for HMSO, D8818935, 9/86, 7102.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.